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(54) THICK FILM INORGANIC OXIDE

(57)Abstract:
PURPOSE: To improve the orientation of an inorganic oxide film by installing one or more intermediate layers for accelerating the crystallization and orientation of the inorganic oxide on a substrate for forming an element and subsequently forming an inorganic oxide film with a specific thickness on the intermediate layer.
CONSTITUTION: An intermediate film of a metal such as Pt is formed on a glass substrate by an EB vacuum deposition method. A coating solution is coated on the intermediate film by spin coating method, etc., followed by thermally drying the coated solution and baking the dried product at a prescribed temperature to obtain the thick film of an inorganic oxide such as PZT having a film thickness of 1-500 μm and a high orientation rate. The coating solution is produced by dissolving a metal salt such as lead acetate and a metal alkoxide such as titanium tetraisopropoxide or zirconium tetrapropoxide in a prescribed weight ratio, mixing the solution with water in an amount equivalent or more to the alkoxy groups and a catalyst such as nitric acid, further mixing the produced partially hydrolyzed gel with the PZT fine particles which are produced by a sol-gel method and which have a critical surface tension of ≤50dyn/cm and an average particle diameter of ≤1 μm, and subsequently dispersing the fine particles with an ultrasonic vibrator.

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CLAIMS

[Claim(s)]
[Claim 1] The thick-film inorganic oxide characterized by preparing at least one or more layers of interlayers who promote crystallization of an inorganic oxide, and orientation-ization on the substrate which forms a component, and forming the inorganic oxide of 1 micrometers or more of thickness in the upper layer.
[Claim 2] A thick-film inorganic oxide is the creation approach of the thick-film inorganic oxide according to claim 1 created by the Sol-Gel method.
[Claim 3] The thick-film inorganic oxide created by the Sol-Gel method is the thick-film inorganic oxide formation approach according to claim 2 characterized by calcinating it after adding the particle which has the same presentation as an inorganic oxide to the partial hydrolysis sol for inorganic oxide formation.
[Claim 4] The particle added to a partial hydrolysis sol is the thick-film inorganic oxide formation approach according to claim 3 which is what is formed from hydrolysis of an organic metal compound.
[Claim 5] The particle which is characterized by calcinating it after the thick-film inorganic oxide created by the Sol-Gel method adds the particle which has the same presentation as an inorganic oxide to the partial hydrolysis sol for inorganic oxide formation, and is added to this partial hydrolysis sol is the thick-film inorganic multiple oxide formation approach according to claim 2 that that critical surface tension is 50 or less dyn/cm, and that mean particle diameter is a thing 1 micrometer or less.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to a thick-film inorganic oxide useful as various components, and its formation approach in the field of electronic ceramics and OPUTO electroceramics.
[0002]
[Description of the Prior Art] The inorganic oxide has the functionality covered in many fields with a presentation, especially, in electronic ceramics and the field of optoelectronics, using inductivity, piezoelectric, pyroelectricity, translucency, and the electro-optical effect, is various and is put in practical use. For example, that by which that for which the thing using a dielectric used piezoelectric as a nonvolatile memory FET component of a low threshold drive used pyroelectricity for the ultrasonic piezoelectric device or the actuator component is used for the infrared sensor etc. Moreover, optical waveguide, an optical switch, a space modulation element, an image memory, etc. are one of translucency and the things using the electro-optical effect, and the application range of a practical use side is very large at them. the former — as the method of producing these ceramics — vacuum deposition, a spatter (JP,63-307606,A), and MOCVD — the thin film is created by the manufacture approaches, such as law (JP,62-67175,A). on the other hand, a bulk object is formed by hot pressing — having — the raw material powder — Sol-Gel with homogeneity sufficient recently — it may create by law (JP,63-35449,A) . The merit of a thin film is being able to form a component / electronic ceramics, and the optoelectronics ceramics on the same substrate. however, in order to realize the various above-mentioned functions, when the thin film of these ceramics applies 1 micrometers or more to an actuator component further, a thick film 100 micrometers or more requires — having — these cases — vacuum deposition, a spatter, and MOCVD — by the thin-film-fabrication approaches, such as law, it is impossible. Moreover, with the bulk object by hot pressing, since the component is destroyed and the processing method which forms a component / electronic ceramics, and the optoelectronics ceramics on the same substrate cannot be done when forming after forming a component on a substrate, constraint will be received in a device.
[0003] Moreover, it has various functions. On a property, when it must be crystallizing, orientation of these inorganic oxides and its thick film may have to be carried out further. For example, it shows a property by carrying out orientation that it is crystallizing piezoelectric material, such as PZT (titanic-acid lead zirconate), to C shaft from the first. It is carrying out polling processing of the ceramic sintered compact generally, and the property is taken out. Polarization processing called this polling is performed by giving the electric field near dielectric breakdown among an about 200-degree C elevated temperature. It will sometimes be destroyed at this time and the increment in a routing counter and the fall of the yield have been a problem.
[0004]
[Problem(s) to be Solved by the Invention] This invention aims at offering the thick-film inorganic oxide with which crystallization or the inorganic oxide which carried out orientation of 1 micrometers or more of thickness is formed on the substrate, and its creation approach.
[0005]

[Means for Solving the Problem] This inventions are the thick-film inorganic oxide characterized by preparing at least one or more layers of interlayers who promote crystallization of an inorganic oxide, and orientation-ization, and forming the inorganic oxide of 1 micrometers or more of thickness on single crystal substrates, such as a substrate which forms a component, i.e., an insulating substrate, and Si wafer, and its manufacture approach.
[0006] This thick-film inorganic oxide performs the various functions of electronic ceramics and the optoelectronics ceramics. the so-called Sol-Gel to which the manufacture approach of the thick-film inorganic oxide manufactures an inorganic oxide by hydrolysis of an organic metal compound, and the polycondensation reaction -- the creation approach of the thick-film inorganic oxide created by law -- it is -- further -- Sol-Gel -- a thick-film inorganic oxide is obtained by calcinating it, after the thick-film inorganic oxide created by law adds the particle which has the same presentation as an inorganic oxide to the partial hydrolysis sol for inorganic oxide formation.
[0007] The Sol-Gel method is the production approach of an inorganic oxide of completing organic metal compounds, such as a metal alkoxide, by the solution system hydrolysis and by carrying out a polycondensation, growing up metal-oxygen-metallic bond, and finally sintering. The description of the Sol-Gel method is that the large area uniformly film is obtained at low substrate temperature. In order to produce a film from a solution furthermore, it excels in adhesion with a substrate. The mixed solution of an organic metal compound equivalent to the metal contained in the multiple oxide specifically obtained finally on a substrate is applied, and it sinters, after carrying out the laminating of the thick film which consists of these inorganic oxides. As an organic metal compound used, alkoxides, acetate compounds, etc. which constitute an inorganic oxide, such as a metaled methoxide, ethoxide, propoxide, and butoxide, are raised. The mineral salt of a nitrate, an oxalate, a perchlorate, etc. is sufficient. Since it is necessary to advance hydrolysis and a polycondensation reaction for producing an inorganic oxide from these compounds, in a spreading solution, addition of water is needed. An addition tends to become uneven [the membraneous quality obtained in order that a reaction may progress quickly, if there are too many additions of the water which changes with systems], and control of a reaction rate is difficult for it. Even if there are too few additions of water, control of a reaction is difficult, and there is optimum dose. A 5 time equivalent mol is desirable from an equivalent mol to the number of association generally hydrolyzed. Furthermore, if a hydrolysis solvent is added, control of a reaction rate and a reaction gestalt can be performed. An acid and a base general as a catalyst are used. Although it is said that an acid catalyst tends to make a linear polymer and a basic catalyst tends to make Motoshige Mitsugi coalesce, it can crawl generally neither on the concentration of the whole solution, nor balance with pH. In the case of this invention, both in-between structure is desirable. As a solvent for addition, the thing excellent in compatibility is desirable. Furthermore, a chelating agent etc. may be added. By applying and annealing such a solution, since an inorganic oxide is amorphous, crystallization starts it. Although sintering temperature changes with ingredients, it is producible at low temperature from the temperature concerning baking of the usual metallic-oxide powder. At an elevated temperature, since there is much what reacts or presentation-changes and changes structurally depending on a device configuration, usabiilty spreads by using this approach. While there was such an advantage, the example of creation by the Sol-Gel method was looked at by only the about 1000A coating film. When carrying out temporary baking from humid gel at desiccation gel, and when sintering from desiccation gel, in order to be accompanied by change of the volume, when thick-film-ization is carried out, the reason may produce a crack and makes thick-film-ization on a substrate difficult. As the crack preventing method, the volume change when changing to desiccation gel from humid gel can improve by adding the particle by the capillary force of a solvent which consists of a firm chemical bond beforehand that what is necessary is to pull and just to make gel association firmer than the force form therefore. That is, prevention of the crack when changing to desiccation gel from humid gel can be performed. In this case, what is necessary is to be based on the capillary force of the solvent produced when changing to desiccation gel from humid gel preferably, to pull, and just to make the force into min. Magnitude deltaP of this capillary force is shown by the formula (1).

[0008]

deltaP=Pr=(2gamma-costheta)/r (1)

r: Radius gamma:surface tension theta of a capillary tube : contact angle [0009] Therefore, by 50 or less dyn/cm, critical surface tension can reduce a contact angle, and can decrease capillary force by the mean particle diameter adding a particle 1 micrometer or less, and prevention of the crack when changing to desiccation gel from humid gel can be performed. Furthermore, in order that there may be no volume change of the added particle also to the volume change when sintering from desiccation gel, a total volume change decreases and it does not result by crack initiation.

[0010] As for this particle, what has the same presentation as an inorganic oxide is desirable. the particle added to a partial hydrolysis sol — the mean particle diameter — 0.5 micrometers or more — it is — too — Sol-Gel — it creates from law. (Generally it is called the hydrolysis precipitation method using an organic metal compound.) When it creates by this technique, particle size, a void content, specific surface area, etc. can be controlled by the heat in which a particle carries out hysteresis. a partial hydrolysis sol and the dispersibility of these particles — Sol-Gel — although created by law, the direction showed very good dispersibility. That is because annealing is given to the same forge fire as the temperature to which the good monodisperse particle of particle size distribution is obtained by the Sol-Gel method, and sintering of about 500 degrees C advances the heat history of a particle, therefore a particle with a big specific surface area can be adjusted low [a void content].

[0011] This invention prepares at least one or more layers of interlayers who promote crystallization of not only creating the thick film of an inorganic oxide but an inorganic oxide, and orientation-ization, condition formation is carried out, and it skips [to which orientation of the thick-film inorganic oxide was carried out on it] a polling process, therefore raises the yield.

[0012] As a thick-film inorganic oxide used by this invention Are the inorganic oxide generally said and it is not limited especially. For example, others [ingredient / which is called the so-called new glass of SiO2 aluminum 2O3, Na2O, and B-2O3 grade / insulating], Piezoelectric ingredients, such as a dielectric ingredient of BaTiO3 and SrTiO3 grade, and Pb(Zr, Ti) O, Half-conductivity ingredients, such as 3O4, BaTiO3, TiO (Ba, Sr)3, SnO2 and ZnO, and MgCr2O4-TiO2 system, (Mn, nickel, Fe, Co) beta-alumina, ZrO2, the conductive (or ion conductivity) ingredient of In2 O-SnO2 grade, Superconductivity ingredients, such as YBa2Cu3O7-delta, O (Zn (Pb, La), Ti)3 and LiNbO3, the polarizability ingredient of LiTaO3 grade, (Pb, Ba, La) The so-called electronic ceramics, such as a magnetic material of OFe (Mn, Zn) 2O3 and BaFe12O19 grade, and the optoelectronics ceramics are raised to Nb 2O6, Nb(Pb, K)2O6, and Nb(Sr, Ba)2O6 pan.

[0013] Moreover, although the thickness of the thick-film inorganic oxide by this invention is thickness required to realize the function and an ingredient differs from the thickness demanded by the device, 1 micrometers or more 500 micrometers or less are shown in common.

[0014] the interlayer who promotes crystallization of an inorganic oxide used by this invention, and orientation -- for example, the thing for which it is the interlayer who takes the value near the lattice constant of the orientation side of the inorganic oxide which should be created, and is making vacuum evaporationo film, such as a metal, deposit on [still like a glass substrate] amorphous, and choosing this metal kind, and a lattice constant is doubled -- it is -- Sol-Gel -- the thick-film orientation film in law is obtained. With vacuum deposition, although this made the metal orientation thin film the interlayer, otherwise, it can be created with a spatter and a CVD method, and an oxide still like ITO(s) (transparence electric conduction film) and aluminum 2O3 other than a metal (for example, a zinc oxide), and SrTiO3 film is sufficient as it. Hereafter, it explains with an example concretely.

[0015]

[Example] The configuration of the sensor section of a piezo electric crystal PZT in a two-dimensional pressure sensor is shown. The block diagram of this device is shown in drawing 1 . Poly-Si TFT (thin film transistor) is constituted on a glass substrate, and the circuit which makes a signal give or drive to stress is constituted.

[0016] After forming SiO2 passivation membrane on a thin film transistor drive circuit, EB vacuum

evaporationo of Pt is performed at the substrate temperature of 350 degrees C. (1000A of thickness) At this time, even if the substrate substrate of Pt is amorphous, it serves as orientation film. Thus, in order to constitute poly-Si TFT on a glass substrate and for a piezo electric crystal to form group bubble **** and the so-called high Brit device in that upper part, TFT will be destroyed in hot pressing and an about 100-micrometer thick film required to change stress into the electrical and electric equipment cannot be created by the vacuum producing-film methods, such as a spatter. Then, it created by the Sol-Gel method of this invention. Hereafter, for simplification, a TFT process is skipped and describes creation of the PZT thick film on SiO2. In addition, this invention is not limited to the following examples, unless the summary is exceeded.
[0017] Titanium 500A and 1000A of platinum were vapor-deposited on SiO2. The solution of the following presentations was applied here using the spinner.
[0018] To one mol of lead acetate, the presentation of coating liquid adjusted titanium tetra-isopropoxide so that it might become 0.5 mols about 0.5 mols and zirconium tetra-propoxide, and it was made to dissolve so that concentration may become methoxy ethanol with 0.5 mol/l, and it added [water] 0.1 mol/l for the nitric acid as -OR radical, and equivalence and a catalyst here. (An organic metal compound is expressed as M(OR) n here.) A partial hydrolysis sol is obtained by controlling an addition rate. Since the crack arose when spreading film production of this partial hydrolysis sol was carried out, in this invention, the PZT particle with a mean particle diameter of 1 micrometer or less was added. This particle adjusts the mixed solution of the same organic metal compound, and adjusts it with a hydrolysis precipitation method. The particle adjusted with this hydrolysis precipitation method is processing the last heat history near sintering temperature (500 degrees C), in particle size distribution, is good and turns into a particle with a large specific surface area low [a void content]. Such a particle addition operation is strengthening the metal-oxygen joint frame formed of sol-gel. Then, distribution by the ultrasonic vibrator was performed. Since specific surface area was large, the mixed solution with a partial hydrolysis sol also with short-time sonication uniform enough was obtained with sufficient particle size distribution. This is used as coating liquid. Although the method of application had technique, such as a spin coat method, the roll coat method, and a dipping method, it performed 2000rpm and spreading for 20 seconds with the spin coat method here. The temperature up of the spreading film was carried out over 30 minutes from a room temperature to 120 degrees C, the hold of 1 hour was carried out, the temperature up was carried out to 600 degrees C over 20 more hours after desiccation of 1 hour at 320 more degrees C, and the PZT thick-film (50 micrometers of thickness) sintered compact was created by holding for 1 hour.
[0019] As a result of X-ray diffraction, when Pt interlayer was employed, the strong stacking tendency was acquired.
[0020]
[Effect of the Invention] By this invention, the thick-film inorganic oxide was made in the large area by formation of homogeneity and the high stacking tendency film on the substrate, i.e., single crystal substrates, such as a glass substrate and Si wafer, which forms a component.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The block diagram of a two-dimensional pressure sensor
[Description of Notations]
1 Glass Substrate
2 TFT Circuit for Drive
3 Stress / Electric Sensing Element
4 Electrode

[Translation done.]